

FUEL PROCESSING OPTIONS FOR PROTON EXCHANGE MEMBRANE FUEL CELL SYSTEMS FOR MOBILE APPLICATIONS

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INTRODUCTION

A fuel cell converts the chemical energy of a fuel directly to DC electricity and will do so continuously as long as a fuel (typically hydrogen or a hydrogen-rich gas) and oxidant (oxygen in air) are fed to it. Hydrogen can be provided in elemental form as a liquid or gas or can be derived by a chemical process from a suitable liquid feedstock such as an alcohol, liquid hydrocarbon or ether. Oxygen is normally available from ambient air or stored in elemental form in specialised applications.

Fuel cells are generally divided into two categories: low and high temperature. Low temperature fuel cells have as an electrolyte, either an acid (Phosphoric Acid - PAFC) or alkaline solution (Potassium Hydroxide - AFC) or a proton conducting membrane which is solid (PEMFC). In high temperature fuel cells, the electrolytes can be molten salts (Molten Carbonate - MCFC) or ion conducting ceramics (Solid Oxide - SOFC).

Of the fuel cell types, PEMFCs are most suitable for transport applications. Although PAFCs are closer to commercialisation, there is little room for major improvements in performance. Efforts are mainly concentrated on cost reduction through mass production. PEMFCs are still in the development phase and offer the possibility of improved performance and reduced costs in the near to middle future. High temperature fuel cells are still in the research and development phase and it will be some considerable time before they become a commercial proposition.

OPTIONS FOR SUPPLY OF HYDROGEN

Hydrogen can be supplied to a PEMFC stack in elemental form using a storage system or as a constituent of a gas stream resulting from the processing of a feedstock such as an alcohol, liquid hydrocarbon or ether. Whilst pure hydrogen produces a better performance from the fuel cell and eliminates the problems of poisoning, hydrogen storage techniques result in physically large systems and introduce logistic problems for refuelling. A number of techniques have been considered including compressed gas, liquid, hydride, glass microspheres, activated carbon and carbon nanofibres. All these techniques have drawbacks which prevent them from being an ideal solution, although the claims for carbon nanofibres, if substantiated could change this assessment.

As a consequence of this situation, much work has been done on fuel processing of alcohols, liquid hydrocarbons or ethers for transport applications. A fuel processor converts a suitable feedstock into a hydrogen-rich gas. The percentage of hydrogen is determined by the technique used. A number of fuel processing techniques have been evaluated for fuel cell applications. These include steam reforming, partial oxidation and autothermal reforming.

PROCESSING OF ALCOHOLS, HYDROCARBONS AND ETHERS

The fuel processor extracts hydrogen from a suitable feedstock. Much work has been done using alcohols such as methanol for transport applications. The

lack of a methanol infrastructure has caused a shift in the direction of liquid hydrocarbons such as gasoline, diesel RFG & LPG. Ethers, such as dimethylether have also been considered.

Carbon monoxide in the reformat feed to a PEMFC decreases the performance dramatically, but reversibly. The typical exit gas from a steam reforming fuel processor contains carbon monoxide at a concentration of 0.3% in approximately 75% hydrogen/25% carbon dioxide. A carbon monoxide concentration of less than 10 ppm is desirable and a concentration less than 2 ppm shows no effect on the performance of a PEMFC at all. Carbon dioxide acts mainly as an inert diluent. However, there is evidence that a certain amount of carbon dioxide is converted *in situ* to carbon monoxide with the consequent affect on performance. Much work has been done on combating the deleterious effect of carbon monoxide on the performance of PEMFC systems. A number of methods have emerged to achieve this:

1. the introduction of a bleed of air/oxygen into the reformat stream;
2. the introduction of a gas clean-up stage between the fuel processor and the anode side of the PEMFC stack;
3. the development of anode electrocatalysts containing ruthenium in addition to platinum to increase carbon monoxide tolerance.

These solutions, both singly and in combination, restore cell performance.

STEAM REFORMING

A hydrogen rich stream can be produced by the steam reforming of hydrocarbons, alcohols or ethers with or without the presence of a catalyst. The use of a catalyst results in lower temperatures and shorter reaction times. The objective of a catalytic steam reforming process is to liberate the maximum quantity of a hydrogen held in the water and feedstock fuel. Carbon in the feedstock is converted into carbon monoxide by oxidation with oxygen supplied in the steam. Hydrogen in the fuel, together with hydrogen in the steam, is released as free hydrogen. The reaction is endothermic. Practically, the reformed gas contains a large percentage of hydrogen, with carbon dioxide, carbon monoxide, methane and unreacted steam. In addition, prior to the reforming stage, it is necessary to remove traces of any components which will poison and deactivate the steam reforming catalyst or the fuel cell anode electrocatalyst. Therefore, as well as the reforming stage, the following steps may be required:

1. feed pre-treatment/desulphurisation;
2. pre-reforming (depending on the feedstock);
3. carbon monoxide conversion to carbon dioxide;
4. preferential oxidation or some other gas clean-up

In situations where low carbon monoxide levels are required, such as for fuel cells, carbon monoxide conversion is often achieved in two stages. The first step takes place as a high temperature shift stage (300-450°C) and the second as a low temperature shift stage (180 - 270°C). Because of the thermodynamics, gas leaving the low temperature shift will still contain a level of carbon monoxide greater than that acceptable for use in the fuel cell. A further stage of catalytic treatment is required to reduce the carbon monoxide level to less than 10 ppm

As an alternative to direct steam reforming, another process configuration which may be adopted is to include a stage of pre-reforming. This system consists of an adiabatic reactor containing a high activity catalyst. The outlet gas from this stage would have a high percentage of methane with other

negligible hydrocarbons present. Such a system operates at a lower temperature (400 - 500°C) than the direct reforming route and enables a lower overall steam to feed ratio to be used. Furthermore, as the gas leaving the pre-reformer is rich in methane, higher levels of preheat can be applied to the reformer feed without risk of cracking and carbon laydown.

PARTIAL OXIDATION REFORMING

Partial oxidation systems rely on the reaction of a hydrocarbon feedstock in a limited supply of oxygen or air to prevent complete oxidation. Traditionally it is carried out without the presence of a catalyst, although catalytic partial oxidation systems are being developed for fuel cell applications. The oxygen is supplied in air. Carbon in the fuel is converted into carbon monoxide whilst the hydrogen in the fuel is released as free hydrogen. The product gas now contains the residual nitrogen from air. Partial oxidation is an exothermic reaction and 17% of the (lower) heat of combustion of the gasoline is released. This raises the temperature of the product gases to approximately 870°C so no external heat source is required. Catalytic partial oxidation attempts to bring about the desired reaction with oxygen using a catalyst. This will enable a lower operating temperature to be used and hence reduce the oxygen consumption. The main difficulty in this area is the development of a durable catalyst which can promote the desired partial oxidation reaction whilst preventing other undesirable reactions from taking place.

AUTOTHERMAL REFORMING

Partial oxidation and steam reforming processes can be combined such that the exothermic partial oxidation reaction heat can be utilised by the endothermic steam reforming reaction. This system is known as autothermal reforming. The partial oxidation and steam reforming reactions can be carried out with or without a catalyst. The use of a catalyst is always accompanied by a potential catalyst poisoning problem by sulphur or lead components in the hydrocarbon or by carbon formation. There is little information in the literature about autothermal reforming of higher hydrocarbons. However, the Johnson-Matthey 'Hot-Spot™' technology has been developed to allow autothermal reforming of methanol. Unlike other autothermal reactors, which require complex heat exchange mechanisms between the exo and endothermic stages, the Hot-Spot™ reactor functions by catalysing steam reforming and partial oxidation on the same catalyst.

'CLEAN-UP' OF FUEL PROCESSING EXIT GAS

The more favoured methods of fuel processing, ie steam reforming, partial oxidation and autothermal reforming, require a further stage of gas processing or 'clean-up' due to the significant quantities of carbon monoxide produced during the processing reactions. The presence of carbon monoxide acts as a severe poison towards the platinum electrocatalyst in the PEMFC at its typical operating temperature of 80°C. Carbon monoxide preferentially adsorbs onto the catalyst surface and thus prevents the hydrogen adsorption necessary for the electrochemical reaction. Carbon monoxide concentrations above 10 ppm are known to cause substantial degradation in PEMFC performance. Ideally the concentration should be no more than 2 ppm. Therefore, it is necessary to include a further stage of gas clean-up prior to the fuel cell to reduce the carbon monoxide concentration to acceptable levels for introduction of the reformat into the cell. A number of processes are available for the removal of carbon monoxide from a gas stream:

1. chemical reduction;
2. membrane separation;
3. water gas shift;

4. chemical oxidation

Chemical reduction of carbon monoxide, ie methanation, is effected over a heterogeneous catalyst such as nickel on alumina at approximately 600°C. However, if large concentrations of carbon monoxide are present then due to the stoichiometry of the reaction there can be a substantial reduction in the hydrogen concentration of the fuel gas.

The use of silver palladium alloy membranes at the fuel processor exit can be used to produce ultra pure hydrogen for the fuel cell. The membrane allows the hydrogen to diffuse through its metallic crystal structure whilst remaining impermeable to the remaining gases produced by the reformation process. Although proven, the technology is at present expensive due to material costs. In addition, the thickness of the membranes (150 microns) necessitates the use of high pressure differentials for the production of acceptable hydrogen flow rates. High parasitic losses are, therefore, placed on the overall system. Research presently underway is focused on developing much thinner membranes (5-25 microns) supported on ceramics. Reductions in cost and operating pressures are, therefore expected without compromising the membrane strength.

The use of a heterogeneous catalyst such as copper/zinc oxide can be used to effect the water gas shift reaction. Since the catalysed reaction is carried out at approximately 200°C, thermal integration with the fuel processor may be possible. The utilisation of the reaction is advantageous since it can increase the hydrogen content of the processed fuel by 30-40%. However, reductions in carbon monoxide concentrations below 20 ppm are not practically possible and, as such, a further stage of gas clean-up is still required.

Finally, carbon monoxide may be selectively oxidised in the presence of hydrogen by air injection into the reformat over a suitable heterogeneous catalyst. Catalytic reactors to date have been used on either packed bed or monolithic designs. Noble metals such as platinum and rhodium (or mixtures of) are particularly active whilst copper based catalysts also show good activity for carbon monoxide oxidation. The reactor operating temperature for the selective oxidation is determined by the catalyst composition, with the reactors showing optimum activity and selectivity within a relatively small temperature range. Close thermal control of the exothermic reaction is therefore necessary to maximise the reaction efficiency.

PRACTICAL FUEL PROCESSING ON BOARD A VEHICLE

Major technical challenges for an integrated fuel processor and fuel cell for a vehicle are as follows:

- Start-up time
- Response to transients
- Methanol quality
- Catalyst deactivation
- Emissions
- Conversion efficiency
- Size
- Cost

It is perceived that for a fuel cell vehicle to be successful in the market place, it will have to perform at least as well as an internal combustion engine vehicle. This means that start up time and response to transient power demands are critical features. At the present time, fuel processors fall short of these goals. The lowest start up times from cold reported are typically several minutes. The quality of the feedstock has an effect on the rate of deactivation of the copper/zinc catalysts traditionally used for steam reforming. The emissions from a fuel cell vehicle with an onboard reformer will not be zero. However, nitrogen oxides and carbon monoxide emissions should be close to zero.

Hydrocarbons and particulate matter should be substantially reduced. There will be no sulphur emission. The emission goal for a fuel cell vehicle with an on-board fuel processor is the Super Ultra Low Emission Vehicle Limit set by California. Conversion efficiency of the feedstock should be as close to 100% as possible. Carryover of unreacted feedstock into a carbon monoxide selective oxidation system affects the performance resulting in an increase in carbon monoxide content of the exit gas. The system efficiency of a PEMFC system incorporating a reformer is predicted to be around 33%. Such a figure should be obtainable over a wide operating range. A reformer for use on-board a vehicle should be as small and light as possible, easy to manufacture using a simple design and cheap materials. The eventual cost target suggested by the motor industry is between \$30/45 per kW.